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(54) **Ink jet recording sheet having an ink-receptive layer containing polyethylene oxide.**

(57) An ink jet recording sheet comprising a support and an ink-receptive layer containing polyethylene oxide and a white filler; in accordance with more preferred embodiments, the layer additionally includes a resin to enhance binding strength and a cationic resin or salt.

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INK JET RECORDING SHEET HAVING INK-RECEPTIVE LAYER CONTAINING PEO

Background of the Invention

The present invention relates to a recording sheet suitable for use in ink jet recording.

Ink jet recording processes have emerged as one of the most important technologies for high speed electronic printing. With their emergence there has arisen a need for recording papers having designed recording properties.

The basic imaging technique in ink jet recording involves the use of one or more ink jet assemblies connected to a source of ink. Each ink jet includes a small orifice which is electromagnetically energized by magnetorestrictive, piezoelectric, thermal, or similar means to emit uniform droplets of ink as a continuous stream or as individual droplets on demand. The droplets are directed onto the surface of a moving web and controlled to form printed characters.

The quality of the record obtained in an ink jet recording process is highly dependent on jet operation and the properties of the ink and the recording paper. The ink must be capable of forming stable ink droplets under pressure and must readily emerge from the ink jet orifice. Aqueous inks containing a water soluble dye and a humectant to prevent the ink from drying out in the jet assembly have been found to be particularly desirable. However, the absorption of these inks by the recording sheet has been somewhat problematic, particularly in the area of multicolor printing where two or more ink drops may overlap on the surface of the recording sheet.

To obtain good image quality, the recording sheet must absorb the ink rapidly and at the same time insolubilize the ink dye on the sheet surface. The former property reduces the tendency for set-off (i.e., transfer of the ink from the paper to sheet handling rollers and the like) whereas the latter property insures that images having high optical density are obtained. Unfortunately, these two properties are in conflict with one another. Papers having high absorbency draw the ink deeply into the paper, and as a result, the optical density of the image formed at the paper surface is reduced. They also suffer from feathering, poor edge acuity, and show-through. Papers with low absorbency, such as highly sized papers, provide good optical density by retaining the ink at the paper surface but have a high tendency to set-off because the ink vehicle is not absorbed rapidly.

The perfect ink jet recording sheet has been described as a plotter with a magic film. The plotter rapidly absorbs the ink vehicle while the magic film insures that the colorant is retained at the surface of the sheet where its light absorbing and reflecting properties are greatest. If the colorant is carried deeply into the paper web, its absorbing strength is reduced, web fibers conduct the ink laterally and poor image sharpness and show-through occurs. See P.A. McManus et al, "Paper Requirements for Color Imaging with Ink Jets", TAPPI, Vol. 66, No. 7, July, 1983, pp. 81-5.

Several types of papers have been proposed for use in ink jet recording. In some cases the basis weight, apparent density and filler content of a paper are adjusted to obtain modified absorption properties (see Japan Kokai 74340/1977 to Jujo Paper Mfg. Co.). In other cases certain

cationic sizing agents, such as cationized petroleum resins, have been added to the paper in the size press to achieve more desirable ink absorption characteristics (see Japan Kokai 109783/1981 to Mitsubishi Paper Mills, Ltd.). Dye absorbing layers containing certain dye mordants have been provided on the surface of the recording sheet in some cases.

Where high quality copies are desired, it has been known to use a paper having an ink receptive layer on the surface thereof. The ink receptive layer is formed of white pigments and an aqueous binder. The pigments enhance the quality of the image by imparting a high level of whiteness to the copy and reflecting incident light and also serve as a substrate which binds the ink jet recording ink. Aqueous binders are used to enhance the absorption of the ink vehicle.

Crooks et al, IBM Technical Disclosure Bulletin, Vol. 21, No. 6, November 1978 discloses a recording paper coated with a layer of a water soluble polymer such as starch, gelatin, polyvinyl pyrrolidone and polyvinyl alcohol.

Maekawa et al, U.S. Patent 4,446,174 describes a recording paper having an ink-receptive layer including a dye-absorbing pigment such as zeolite, clay, attapulgite, and diatomaceous earth and a binder. A number of binders are disclosed in the patent including binders having dissociable dye-absorbing groups such as polyacrylates, styrene-maleic annydride copolymer, sodium alginate, ethylene-maleic anhydride copolymer and cationic starch; and binders not having dissociable groups such as starch, polyvinyl alcohol, polyvinyl pyrrolidone and styrene-butadiene latex.

Murakami et al, U.S. Patent 4,425,405 discloses an ink-jet recording sheet in which the ink receptive layer contains polyvinylpyrrolidone and/or vinylpyrrolidone-vinyl acetate copolymer and a white filler. Optionally the layer may also include a water insoluble binder to impart moisture resistance.

Ink jet recording papers are also known in which the dye-absorbing characteristics of the paper itself are beneficially modified by incorporating certain polymers or sizing agents into the paper itself. Maekawa et al, U.S. Patent 4,308,542, and Minagawa, U.S. Patent 4,269,891 describe ink jet recording papers prepared from synthetic paper. The papers are designed to enable viewing the images by reflection or by transmission of light through the recording sheet. Certain water soluble adhesives having a highly hydrophilic characters, including among them polyethylene oxide, are added to the pulp to improve surface strength and improve the ink absorption properties.

While there are numerous examples of ink jet recording papers in the art, there is a need for alternative papers and there is particularly a need for coated papers suitable in high quality printing.

Summary of the Invention

It is one object of the present invention to provide an ink jet recording paper useful in high quality printing applications.

It is another object of the present invention to provide an ink jet recording paper having an ink-receptive layer containing a white pigment and a binder which exhibits excellent ink receptivity and is able to control ink dot spreading (i.e., size and uniformity).

It is a further object of the present invention to provide an ink jet recording paper having an ink-receptive layer containing a pigment and a binder which exhibits less tack at high moisture/humidity levels and provides waterfastness.

Still another object of the present invention is to provide a pigmented ink jet recording layer that is useful with both aqueous and solvent based inks.

These and other objects are achieved in accordance with the present invention which provides an ink jet recording paper comprising a paper support and an ink-receptive coating on at least one surface of said support, said ink-receptive coating including a white pigment dispersed in polyethylene oxide.

Detailed Description of the Invention

The ink-absorptive qualities of the paper of the present invention will vary with the amount and the molecular weight of the polyethylene oxide incorporated into the ink-receptive layer as well as other factors such as the nature of the pigment, the presence of other additives, and the manner of coating. The ink-receptive layer used in the present invention in its simplest form includes a white pigment and polyethylene oxide. However, polyethylene oxide does not provide sufficient binding strength to satisfy all the requirements of the recording process. Ink receptive layers consisting of polyethylene oxide and pigment tend to dust, i.e., lose pigment more readily and sometimes crack. For this reason it is preferred to include an additional resin in the composition to ennance binding strength and thereby reduce dusting and improve the integrity of the layer.

The molecular weight of the polyethylene oxide used in the present invention may range from about 100,000 to 900,000 and preferably from about 100,000 to 300,000.

Suitable resins useful in enhancing the binding strength of polyethylene oxide can be selected from among a number of high molecular materials conventionally used in papers or paper coatings. A binder should be selected which is compatible with the polyethylene oxide. Representative examples of useful polymers include polyvinyl acetate, ethylene-vinyl acetate copolymer, polymethacrylates, polyacrylates, polyvinyl alcohol, oxidized starch, carboxymethyl cellulose, hydroxyethyl cellulose, styrene-maleic acid copolymer, styrene-butadiene copolymer and the like. Polyvinyl alcohol and starch are usually used because they are relatively inexpensive and they provide good binding strength.

The polyethylene oxide is usually used in the ink-receptive layer in an amount of about 5 to 70% by weight and preferably 10 to 40% by weight based on the dry weight of the ink-receptive layer. The amount of other resin included in the ink-receptive layer to enhance binding strength will vary with its nature, the amount and nature of the filler used and other factors. Typically, these other resins may be incorporated into the coating in an amount of about 0 to 60% by weight (dry) or in weight ratio to the polyethylene oxide of about 1:10 to 10:1.

Examples of fillers which can be used in the practice of the invention in combination with polyethylene oxide include clay, talc, calcium carbonate, alumina and alumina hydrate, zeolite, synthetic silica, calcium sulfate, diatomaceous earth, magnesium silicate, barium carbonate, barium sulfate, aluminum silicate, magnesium

oxide, magnesium carbonate, calcium silicate, satin white, etc. The preferred filler is synthetic silica (e.g., Syloid 244 from W. R. Grace Co.). It may be desirable to dilute the silica with another white filler in some cases. The filler is generally used in an amount of about 5 to 90% and preferably 40 to 90% by weight based on the dry weight of the recording layer.

The recording characteristics of the ink jet recording paper of the present invention are generally improved by the addition of a cationic resin and/or polyvalent metal salt. In most applications, aqueous ink compositions containing acid or direct dyes are used in ink jet recording. These dyes advantageously react with the cations provided by the resin or the metal salt and become more rapidly set in the ink receptive layer. This tends to prevent off-set and further reduce feathering and dot spread.

Useful cationic polymers are characterized by a high cationic character. Such polymers are typically made up of at least 3 mol % cationic monomer units and preferably at least 10 mol % and up to 100%. Polymeric amines such as polymers of quaternary amines or amines converted to quaternary amines under acid conditions can be used. The cationic character of these polymers can be expressed as a nitrogen concentration since the nitrogen present in the polymers generally is in the form of cationic quaternary ammonium groups. Thus, the polymeric cationic amines used in the present invention can be characterized as having a nitrogen content in excess of about 0.1%, preferably in excess of 1.5% and still more preferably in excess of 3.0% by weight.

A useful class of cationic polymers are so-called electroconductive polymers which are conventionally used in electrophotographic, electrographic or electrostatographic processes. Examples of such polymers are described in U.S. Patents 3,011,918; 3,544,318; 4,148,639; 4,171,417; 4,316,943; and 3,813,264. Tnese polymers are characterized by the presence of a high percentage of cationic groups such as tertiary amino and quaternary ammonium cationic groups. Representative polymers are nomopolymers or copolymers of cationic monomers such as quaternary diallyldiakylammonium chlorides such as diallyldimethylammonium chloride, N-alkylammonium chlorides, methacrylamidopropyltrimethylammonium chloride, methacryloxyethyl trimetnylammonium chloride, 2-hydroxy-3-methacryloxypropyl trimethylammonium chloride, methacryloxyethyl trimethylammonium methosulfate, vinylbenzyl trimetnylammonium chloride and quaternized 4-vinylpyridine.

Representative examples of commercially available cationic polymers that are useful in the present invention are Warcofix 808 (a guanidine-formaldehyde polymer available from Sun Chemical Corp.), Calgon 261 LV and Calgon Conductive Polymer 7091 RV (polydimetnydiallylammonium chlorides available from Calgon Corp.), Nalco 8674 (a cationic polyamine available from Nalco Corp.), and CAT Floc C (available from Calgon Corp.).

Tne polyvalent metal salts used in the present invention are polyvalent water soluble salts of polyvalent cations from Group II, Group III or the Transition Metals of the Periodic Table of Elements. Typically, these salts can be dissolved in water in an amount greater than 5 g/100ml at 23°C. Tne most readily available and cost effective salts are Zn^{2+}, Al^{3+}, Mg^{2+}, Ca^{2+} and Ba^{2+} salts.

Salts which tend to color the paper such as Fe^{2+}, Fe^{3+}, and Cu^{2+}, while functional, must be used in limited amounts or not at all. Preferably, the salts are salts of one of the aforesaid polyvalent cations and an anion of a weak acid such as an anion of an acid having a pKa value greater than 2.0 and, more preferably, greater than 3.0. Salts of strong acid anions such as alum are capable of insolubilizing an ink jet dye but are generally undesirable because they impart high acidity to the paper which accelerates degradation. Thus, while chlorides, sulfates, chlorates, and nitrates are useful, the preferred salts are acetates, formates, chlorohydrates, malonates, succinates, and salts of other weak organic acids.

Specific examples of salts useful in the present invention are alum, calcium formate, and aluminum chlorohydrate. Certain zirconium Zr^{3+}, Zr^{4+}, and Zr^{5+} salts are also believed to be useful such as zirconium oxychloride and zirconium hydroxychloride.

The ink-receptive layer of the present invention may contain about 5 to 50% by weight of the aforementioned cationic resins and/or about 1 to 25% by weight of the polyvalent metal salt.

The ink-receptive layer is typically formed by preparing an aqueous dispersion of polyethylene oxide, filler and any other additive(s) and coating it onto a support in a conventional manner. Conventional paper coating machines such as blade coaters, air knife coaters, roll coaters, brush coaters, gravure coaters, size presses, rod coaters, and curtain coaters may be used for this purpose. The coating composition may be applied to the support in an amount of about 1 to 40 g/m^2 on a dry basis and preferably 5 to 20 g/m^2. The upper limit on

the thickness is not as critical. After the coating is dried it may be smoothed by calendering if desired.

In general, there are no restrictions on the type of paper that may support an ink-receptive layer in accordance with the present invention. Any restrictions on the paper support typically are a product of the recording application or the recording apparatus rather than the coating composition. For most applications, papers having a basis weight of about 12 to 30 pounds per 1300 sq. ft., an apparent density in the range of 0.3 to 1.2 and filler content of 0 to 40% are useful. In general, conventional bleached Kraft and bleached sulfite pulps can be used in the present invention. Waterleaf, low size, high size and bond paper can be used. The coating can also be used with certain synthetic papers or applied to polymeric films.

The preferred support thickness is about 30 to 150 microns.

Representative examples of thermoplastic films which can be used in the present invention include polyester films such as polyethylene terephthalate, polystyrene, polyvinyl chloride, polymetnylmethacrylate and cellulose acetate.

The ink jet recording paper of the present invention is preferably used in conjunction with aqueous ink jet recording inks but it can also be used with certain solvent-based inks. Representative examples of useful dyes include acid dyes such as Tartrazine (CI 19140), Quinoline Yellow (CI 47005), Eosin (CI 45380), Erythrosine (CI 45430), Brilliant Cyanine 6B (CI 42660), Acid Black 1 (CI 20470), Acid Black 36 (CI 27275) and Acid Blue Black 10B (CI 20470), Acid Blue 193 (CI 15707), Acid Blue 194 (CI 17941), Acid Blue 249 (CI 74220); and direct dyes such

as Direct Black 19, Direct Black 49, Direct Black 56, Direct Black 74, Direct Black 103, Direct Black GW, Capamine Black ESA, Deep Black XA (CI Direct Black 154), Black G (CI 35255), Pnthalocyanine Blue (CI 74180), Direct Blue 78, Direct Blue 239, Direct Blue 120, Direct Blue 110, Direct Blue 19, Direct Scarlet 4BS (CI 29160). The CI number in the description above indicates the identification number in the Color Index, 3rd Edition, the Society of Dyers and Colorists, Bradford, Yorkshire (1971).

The present invention will be illustrated in more detail by the following non-limiting examples:

Example 1

A coating composition was prepared by combining the following:

	% Solids (in water)
Polyvinyl alcohol (Elvanol 71-30, E.I. DuPont Co.)	12
Polyethylene oxide (molecular weight 200,000)	100
Synthetic Silica (Syloid 244 W.R. Grace Co.)	12.5
Barium sulfate	54.0

The coating was drawn down on a hard size raw stock using a 0.5 ml bird bar. As dried, the ink-receptive layer contained 12.5% polyvinyl alcohol, 12.5% polyethylene oxide, 25% aluminum silicate and 50% barium sulfate. When a commercially available acid magenta recording ink was applied to the layer with a fountain pen, the ink displayed no tendency to feather.

Example 2

Three ink jet recording papers were prepared as in Example 1 except the molecular weight of the polyethylene oxide was varied. Sample A was prepared using a 100,000 molecular weight polyetnylene oxide. Sample B was prepared using a 200,000 molecular weight polyethylene oxide and Sample C was prepared using a 300,000 molecular weight polyethylene oxide. A solvent based magenta recording ink was applied to the ink-receptive layer of each of tne sneets with an Advanced Color Technology ACT-1 Printer. Tne dot area, parameter and shape were measured. Tne results are shown in Taole I. For comparison, dot size is shown for the same ink as applied to a commercial pond paper.

Table I

Sample	Mean area (μ^2)	Mean Parameter (μ)	Shape Factor
A	63055	944	1.06
B	73020	1048	1.09
C	75172	1128	1.16
Commercial Ink Jet Paper	85627	2462	2.41

Example 3

Ink jet recording papers were prepared by coating the compositions shown in Table 2 below on a commercial rawstock using a rod coater. Samples 1-3 correspond to samples prepared according to the teachings in U.S. Patent 4,425,405 containing polyvinyl pyrrolidone in the ink-receptive layer. Samples 4-6 are papers prepared in accordance with the present invention.

Table II

Sample	Ct. Wgt. g/m^2	PVP[5] %	PEO[3] %	PVA[2] %	Syloid[1] %	Baryta %	Warcofix 808[4] % Coating[6]	Aluminum Chlorohydrate % Coating[6]
1	7.2	12.5		12.5	25	50	7	3
2	8.8	12.5		12.5	25	50	7	3
3	10.8	12.5		12.5	25	50	7	3
4	4.1		12.5	17.5	20	50	7	3
5	6.9		12.5	17.5	20	50	7	3
6	8.1		12.5	17.5	20	50	7	3

1) Davison Chemical Division, W. R. Grace & Co.
2) Elvanol 71-30, E.I. Dupont de Nemours Co.
3) Polyox WSR N-10, Union Carbide Corp.
4) Sun Chemical Co.
5) Polyvinyl pyrrolidone, 360,000 molecular weight
6) Amt by weight based on balance of composition

Images were formed on each of the sheets using commercially available aqueous based cyan, magenta, yellow and black ink jet recording inks and a solvent-based magenta ink and the optical density was measured. The results are shown in Table 3 from which it can be seen that the polyethylene oxide based recording layer in accordance with the present invention performs at least as well as recording layers containing polyvinyl pyrrolidone.

Table III

Optical Density

Sample	Yellow	Magenta	Cyan	Black	Solvent Based Magenta
1	0.70	1.18	1.40	1.45	0.91
2	0.69	1.14	1.27	1.32	0.86
3	0.66	1.02	1.21	1.23	0.72
4	0.73	1.19	1.26	1.43	0.94
5	0.71	1.16	1.29	1.42	0.82
6	0.65	1.06	1.23	1.31	0.79

Having described the invention in detail and by reference to specific embodiments thereof it will be apparent that modifications and variations are possible without departing from the scope of the following claims:

CLAIMS

1. An ink jet recording paper comprising a support and an ink-receptive coating provided on at least one surface thereof, said coating including a white pigment and polyethylene oxide.

2. The ink jet recording paper of claim 1 where, in addition to said polyethylene oxide, said coating includes a resin which is compatible with polyethylene oxide and which enhances binding strength.

3. The ink jet recording paper of claim 2 wherein said resin is selected from the group consisting of polyvinyl acetate, ethylene-vinyl acetate copolymer, polymethacrylates, polyacrylates, polyvinyl alconol, oxidized starch, carboxymethyl cellulose, hydroxyethyl cellulose, styrene-butadiene copolymer and styrene-maleic acid copolymer.

4. The ink jet recording paper of claim 3 wherein said white filler is selected from the group consisting of clay, talc, calcium carbonate, calcium sulfate, diatomaceous earth, magnesium silicate, barium carbonate, aluminum silicate, magnesium oxide, magnesium carbonate, calcium silicate, satin white, synthetic silica and alumina.

5. The ink jet recording paper of claim 4 wherein said filler is present in said coating in an amount of about 5 to 90% by weight.

6. The ink jet recording paper of claim 5 wherein the weight ratio of said resin to said polyethylene oxide is about 1:10 to 10:1.

7. The ink jet recording paper of claim 1 wherein said polyethylene oxide has a molecular weight in the range of about 100,000 to 300,000.

8. The ink jet recording paper of claim 7 wherein said white filler is a synthetic silica.

9. The ink jet recording paper of claim 2 wherein said resin is polyvinyl alcohol.

10. The ink jet recording paper of claim 1 wherein said support is selected from the group consisting of waterleaf, low size, high size or bond paper.

11. The ink jet recording paper of claim 1 wherein said support is paper.

12. The ink jet recording paper of claim 1 wherein said ink-receptive coating is calendered.

13. The ink jet recording paper of claim 1 wherein said ink-receptive coating comprises polyethylene oxide, polyvinyl alcohol, and synthetic silica.

14. The ink jet recording paper of claim 2 wherein said ink-receptive coating additionally includes a cationic resin.

15. The ink jet recording paper of claim 2 wherein said ink-receptive coating additionally includes a polyvalent metal salt.

16. The ink jet recording paper of claim 14 wherein said cationic resin is a polymeric amine.

17. The ink jet recording paper of claim 15 wherein said salt is a salt of Zn^{2+}, Al^{3+}, Mg^{2+}, Ca^{2+} or Ba^{2+}.

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EUROPEAN SEARCH REPORT

0199874

Application number

EP 85 30 8392

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl 4)
X,Y	US-A-4 102 845 (G. SCHRÖDER et al.) * Whole document *	1-6,11,12	B 41 M 1/36 D 21 H 1/28
X,Y	US-A-3 812 072 (A. KÜHLKAMP et al.) * Columns 1-3; column 4, lines 34-75; column 7, lines 61-70; column 9, table 4 *	1-6,9-12	
Y	GB-A-2 050 866 (FUJI PHOTO FILM CO.) * Claims 1-4,9,12-14 *	1,4,5,10-12	
Y	DE-A-3 132 248 (FUJI PHOTO FILM) * Claims 1,11; page 32, line 4 - page 33, line 9 *	1-4,9-12	
A		8,14	TECHNICAL FIELDS SEARCHED (Int Cl 4) B 41 M D 21 H
D,A	US-A-4 446 174 (M. MACKAWA et al.) * Column 4, line 32 - column 8, line 5 *	3-5,8-12,14,15	
E	EP-A-0 164 196 (THE MEAD CORP.) * Whole document *	1,4,10-12,14,15	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	28-05-1986	NESTBY K.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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